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Recrystallisation of Supersaturated Copper-Cobalt Solid Solutions

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The mutual influence of precipitation and recrystallisation was investigated in supersaturated and cold worked Cu-Co-alloys. For medium amounts of deformation (10 to 20% for 2.8 at. % Co) a discontinuous reaction was found that leads to simultaneous annihilation of dislocations and formation of rows of Co-particles. At lower amounts of deformation, recrystallisation is inhibited by particles, while recrystallisation is complete before precipitation starts at higher amounts of deformation.

1. Introduction

Recrystallisation of highly deformed metals occurs by formation and motion of grain-boundaries. In areas with high curvature of lattice, e.g. at deformation bands, dislocations rearrange and form new grain-boundaries, which are able to move as a reaction front into the deformed material, annihilating the dislocations. After small amounts of deformation ($\lesssim 3\%$) recrystallisation can occur exclusively by motion of the original grain-boundaries. The temperature-dependence for the start of recrystallisation (assuming a constant size of the recrystallisation nuclei) follows an Arrhenius type equation:

$$t_R = A(N) \exp \frac{Q(N)}{kT},$$

t_R is the incubation period before the start of recrystallisation; $A(N)$ is a constant factor which contains the driving force for the reaction, the entropy term and the geometrical factors; N is the dislocation density; $Q(N)$ is the energy of activation for the formation of a mobile reaction front and has the order of magnitude of Q_0 (activation energy for self-diffusion) and corresponds to the activation energy for motion of dislocation nodes. $Q(N)$ decreases with increasing dislocation density. In case dislocation arrangements lead to long-range stresses inside the material, a value $Q(N) < Q_0$ can be expected.

Dissolved atoms can influence recrystallisation in different ways:

(a) By changing the stacking fault energy, a change in the dislocation arrangement in the deformed material is caused. This leads to a change in driving force and internal stress distribution.

(b) Segregation at dislocations leads to the retardation of the rearrangement of dislocations and in this way to a delay in the start of recrystallisation. The activation energy $Q(N)$ is increased by an amount equivalent to the energy of interaction between the dislocations and foreign atoms.

(c) Segregation at grain-boundaries leads to a decrease in grain-boundary mobility and to less anisotropy of mobility.

In addition to these factors, recrystallisation of supersaturated solid solutions is affected by precipitation of particles. These effects have been summarised recently [1]. They will be discussed using fig. 1. The start of precipitation follows the equation

$$t_P = B \exp \frac{Q_B + \triangle G_K(T)}{kT},$$

where t_P = incubation period until start of precipitation, B = factor containing the driving force (supersaturation), the entropy term and geometrical terms (diffusion paths), Q_B =

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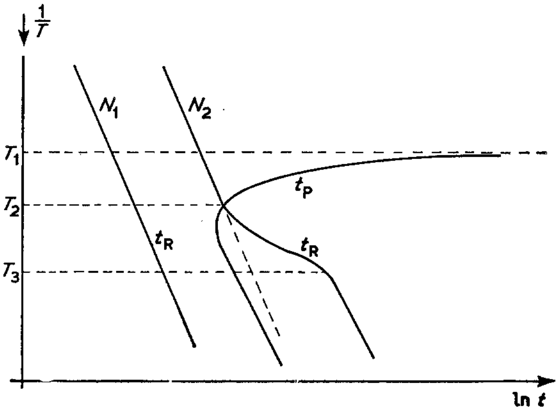


Figure 1 Schematic diagram showing the temperature-dependence of incubation periods for precipitation (t_P) and recrystallisation (t_R), *concn.* = constant. Dislocation density N_1: no mutual influence of both processes; dislocation density $N_2 < N_1$: $T > T_2$, discontinuous recrystallisation of the homogeneous solid solution; $T_2 > T > T_3$, discontinuous recrystallisation influenced by precipitation; $T < T_3$, continuous recrystallisation. Rearrangement of dislocations is controlled by coarsening of particles.

activation energy for diffusion of the dissolved atoms; $\triangle G_K$, the activation energy for nucleation of the second phase, depends on the undercooling and varies from infinity at the equilibrium temperature T_1 to extremely small values for large undercooling.

In the case when $t_P \gg t_R$ (dislocation density N_1) recrystallisation is already completed before precipitation starts. Consequently the two processes do not affect each other.

In the case when $t_P \lessapprox t_R$ (dislocation density N_2) different processes can be expected in different temperature ranges. In the range $T_1 > T > T_2$ grain-boundaries still originate and move in the supersaturated solid solutions. At $T < T_2$ the motion of grain-boundaries is retarded by precipitating particles. The particles can either be dissolved at the grain-boundaries or bypassed as obstacles. In the range $T_2 > T > T_3$ rearrangement of dislocations for the formation of recrystallisation fronts and their mobility is retarded increasingly with increasing supersaturation. Below T_3 the particle density is so high that all dislocations are pinned. Rearrangement of dislocations for the formation of grain-boundaries can only occur simultaneously with the coarsening of the particles, and no grain-boundaries can move (continuous recrystallisation).

The purpose of this work is to investigate the recrystallisation behaviour, as a function of dislocation density and supersaturation of the solute atoms, in a simple alloy system. Copper-cobalt alloys have been chosen, because the precipitation behaviour of these alloys is well known [2–4]. From the supersaturated copper solid solution cobalt precipitates with about 10 at. % copper in solution above 340° C as a fcc solid solution in the form of small particles. These particles have a statistical local distribution in the matrix. They grow to a size of 1000Å as spheres. At a size of 500 Å a transition from coherent to incoherent interfacial structure occurs. The energy of interaction between cobalt atoms and dislocations is small (0.04 eV); the lattice parameters of matrix and particles differ by less than 2%. Segregation of cobalt atoms at dislocations and grain-boundaries is expected to be small. There is no strong preference for nucleation at dislocations. Discontinuous precipitation has not been observed.

2. Experimental Procedure

Alloys with the following cobalt contents were vacuum-melted from 99.95% copper and 99.95% cobalt.

alloy 1	Cu + 0.1 at. % Co
alloy 2	Cu + 0.4 at. % Co
alloy 3	Cu + 1.1 at. % Co
alloy 4	Cu + 2.8 at. % Co

These alloys were homogenised in an evacuated quartz tube at 1000° C and water-quenched. The homogeneous solid solutions were rolled at room temperatures. The amounts of rolling varied between 3 and 90% ($\epsilon \triangleq$ reduction in area). Start and finish of recrystallisation were determined by light microscopy. Transmission electron microscopy was used for observation of the microscopic interactions between precipitation and rearrangement of dislocations. Start of precipitation was defined by the occurrence of particles visible in the electron microscope (50 Å diameter).

3. Experimental Results

In the highly deformed samples ($\epsilon = 90\%$) start of recrystallisation t_R was retarded with increasing alloy content. Nevertheless t_R follows an Arrhenius plot in the temperature range investigated. From the observed temperature-dependence the following activation energies are deduced for the different alloys:

pure copper	(1.0 ± 0.2) eV
alloy 2	(1.5 ± 0.2) eV
alloy 3	(1.4 ± 0.2) eV
alloy 4	(2.4 ± 0.2) eV

The recrystallised grains form preferentially at deformation bands and at the original grain-boundaries. After deformation of $20\% < \epsilon < 30\%$ new recrystallised grains originate at the original grain-boundaries. They grow into the deformed matrix. At small amounts of deformation ($< 20\%$) only the original grain-boundaries move. In alloy 4, bulging of the grain-boundaries can be observed. At the same grain-boundary the bulges move in different directions (arrow in fig. 2a). During ageing of homogeneous solid solutions of alloy 1 deformed to the same amount these bulges do not occur (fig. 2b).

In fig. 3 the fraction n of the recrystallised grains that formed at original grain-boundaries has been plotted as a function of the amount of deformation. For different amounts of deformation ageing temperatures were chosen which led to comparable stages of recrystallisation (30%/400° C; 50%/300° C; 90%/180° C).

Start, t_R, and completion, t_{RE}, of recrystallisation as well as the start of precipitation t_P were determined for alloy 4 and $\epsilon = 90\%$ and plotted in a time-temperature-reaction diagram (fig. 4). From the straight portions of the curve t_P at high supersaturation the activation energy for start of precipitation is calculated as 2.2 ± 0.2eV. (The activation energy for diffusion of cobalt atoms in copper = 2.3 eV [5].) No preferred nucleation at dislocations was observed. The particles form only after the recrystallisation is completed. Fig. 5 shows the microstructure of this alloy after a long period of ageing.

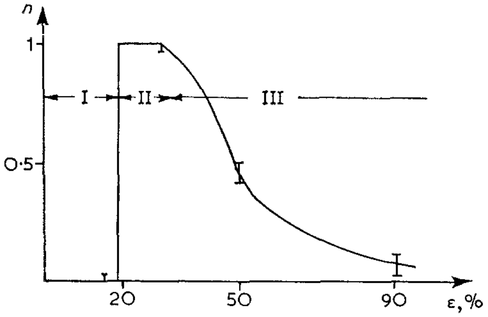
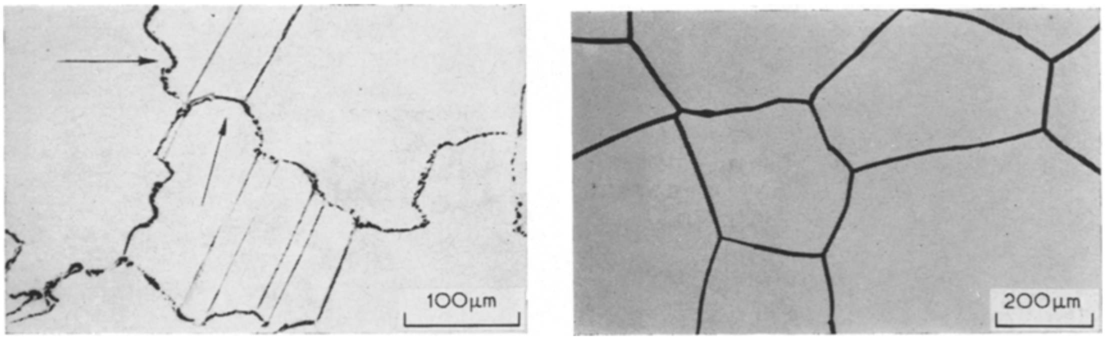


Figure 3 Number of recrystallised grains which have formed at original grain-boundaries as fraction n of total number of recrystallised grains. I: motion of original grain-boundaries. II: formation of recrystallised grains in the environment of original grain-boundaries. III: formation of recrystallised grains in the environment of original grain-boundaries and in the interior of original grains. Cu + 2.8 at. % Co. For heat-treatments see under Section 3.

In alloy 4, deformed between 10 and 20% and aged in the temperature range between 450 and 600° C, a special type of discontinuous precipitation occurs. Fig. 6 shows the different stages of this process, in which the particles become arranged as chains perpendicular to the reaction front. Simultaneously the dislocation density decreases ($N_1 \approx 10^{10}$ cm^{-2} to $N_2 \approx 10^8$ cm^{-2}). At higher ($> 20\%$) and smaller ($< 10\%$) amounts of deformation discontinuous precipitation was not observed.

In the samples of alloy 4, deformed less than 10%, the precipitating particles inhibit rearrange-



(a) (b)

Figure 2 Behaviour of grain-boundaries during ageing after small amounts of deformation. (a) Bulging of the original grain-boundaries. Cu + 2.8 at. %, 10% deformed, 100 h 550° C. (b) No bulges. Cu + 0.1 at. % Co, 10% deformed, 100 h 550° C.

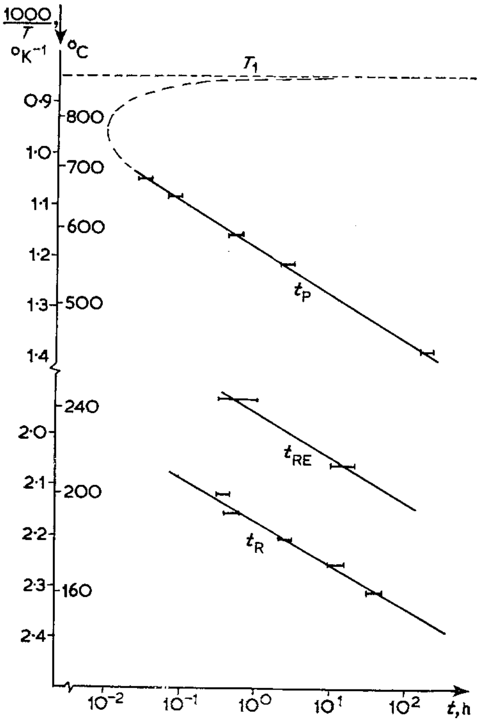


Figure 4 Time-temperature-reaction diagram. Cu + 2.8 at. % Co, 90% deformed. Recrystallisation is completed before precipitation starts. Energy of activation for start of recrystallisation = 2.4 eV.

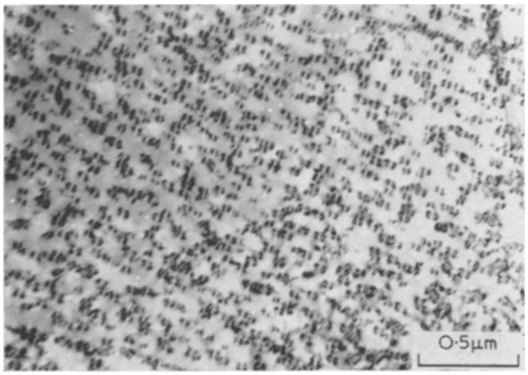


Figure 5 Precipitation after complete recrystallisation, leads to statistical distribution of particles. Cu + 2.8 at. % Co, 90% deformed, 300 h 550°C (× 27 500).

ment of dislocations as well as the motion of grain-boundaries (fig. 7a, 7b.)

4. Discussion

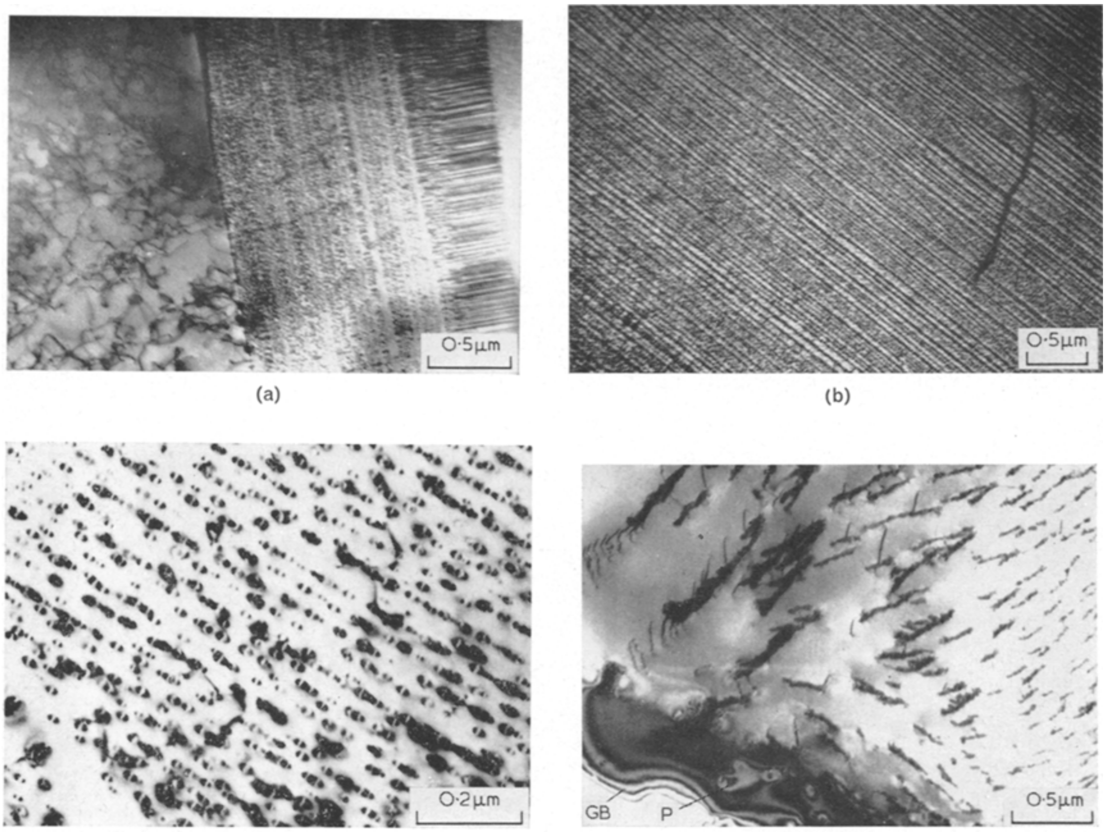
For the interpretation of the observed phenomena the following factors are important:

(i) The induction periods for the different reactions, t_P, t_R. Only if $t_P/t_R \lesssim 1$, does interaction of precipitation and recrystallisation occur.
(ii) The forces acting on the grain-boundaries. If a mobile grain-boundary is present, it can only move if $\Sigma P_i > 0$.
The driving force ΣP_i can be calculated from the decrease in free energy per unit volume swept by the grain-boundary. The free energy decreases (a) if the grain-boundary migrates into an area with high dislocation density N_1. Dislocations are annihilated and $P_N \approx \mu b^2 (N_1 - N_2)$; μ = shear modulus; b = Burgers vector; N_2 = dislocation density behind the moving grain-boundary; (b) if the grain-boundary, moving as a reaction front, catalyses precipitation of a second phase, then $P_C \approx \nu_m RT \ln c_0/c_1$ (assuming an ideal solid solution); c_0 = concentration of the supersaturated solid solution; c_1 = equilibrium concentration; ν_m = mole number.

The "pinning force" of the particles acts in the opposite direction. According to Zener [6] $P_P = 3f/2r\ \gamma_{GB}$, where it is assumed that the particles are thermodynamically stable with respect to the grain-boundary and statistically distributed in the matrix, and f = precipitated volume portion; r = particle radius; γ_{GB} = energy of grain-boundary.

These forces are time-dependent at constant temperature. They are lowered by the following process: P_N by recovery (decrease in dislocation density), P_C by decomposition in front of the reaction front, P_P by coarsening of particles (increase of r at constant volume fraction f).

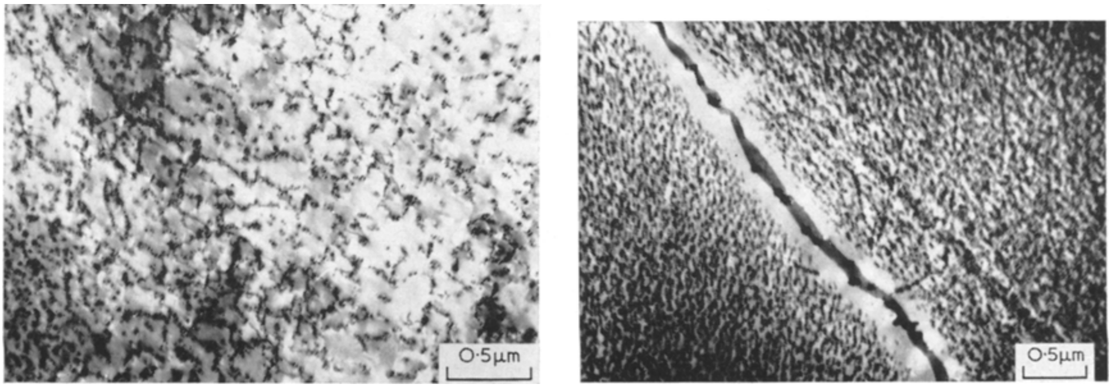
Because no preferred nucleation at dislocations occurs in this particular alloy, t_P and P_P can be regarded as independent of dislocation density N. t_R decreases with increasing dislocation density, while P_N increases. Therefore, the following combinations are possible:
(i) $t_R \ll t_P$, the case of no interaction between recrystallisation and precipitation at high dislocation densities (high degrees of deformation). The recrystallisation front moves under the influence of driving force P_N through the deformed and supersaturated solid solution. This case has been observed in the 90% deformed alloys (fig. 4). Recrystallisation is only influenced by the dissolved cobalt atoms. They have the effect of leading to a more even distribution of dislocation during plastic deformation as compared to the situation in pure copper. The long-range stress fields which favour for pure copper



(a) (b)

(c) (d)

Figure 6 Discontinuous precipitation in Cu + 2.8 at. % Co. (a) Start of discontinuous precipitation. A grain-boundary moves as a reaction front into deformed and supersaturated matrix (left hand side) (× 22000). (b, c) Particles form as chains by coagulation of rods after discontinuous precipitation, 10% deformed 10 h and 100 h 550° C. (b × 16 500), (c × 66 000). (d) Discontinuous reaction is stopped by particles (P) precipitated in front of the reaction front (GB), 14% deformed, 100 h 550° C (× 22000).



(a) (b)

Figure 7 (a) Precipitated particles prevent the rearrangement of dislocations. Cu + 2.8 at. % Co, 5% deformed 100 h 550° C (×22 000). (b) Grain-boundaries are pinned by particles. Cu + 2.8 at. % Co, 5% deformed, 300 h 550° C (×16 500).

the rearrangement of dislocations to grain-boundaries are therefore weaker. Correspondingly, the activation energy for start of recrystallisation increases. In alloy 4 $Q(N)$ approaches Q_0.
(ii) $t_R \geq t_P$. For small dislocation densities $t_R > t_P$ and $P_N < P_P$ are to be expected. The grain-boundaries are pinned by particles (alloy 4, $0 \leq \epsilon < 10\%$, fig. 7b). For higher dislocation densities $P_N > P_P$. Particles lead to a retardation of the rate of recrystallisation as compared to the homogeneous solid solution. The transition from $t_R < t_P$ to $t_R > t_P$ in fig. 1, curve N_2, occurs at a sharp temperature only for the beginning of the recrystallisation reaction. Depending on the spacing of the nuclei this reaction has to sweep a certain path and reaches the interior of the grain at a time $t_R + \triangle t$. During the time interval $\triangle t$, precipitation and recovery take place ahead of the reaction front and therefore the driving force ΣP_i changes. The changes in the mode of the reaction therefore take place in a temperature range $\triangle T$ below T_1 and above T_2. Above T_2 the reaction can start sweeping into the supersaturated solid solution. After the recrystallisation reaction has travelled a certain path, precipitation starts and the velocity of the reaction front decreases owing to the force P_P. Correspondingly a reaction front that started at a temperature not too high above T_2 stops, if owing to continued precipitation the condition $\Sigma P_i \leq 0$ is fulfilled. From then on only continuous recrystallisation can continue and a mixed microstructure results. The recrystallised volume fraction increases for certain ageing conditions, with increasing dislocation density, for the following reasons: (a) increase of P_N and therefore an increase of the grain-boundary velocity; (b) increase in the density of recrystallisation nuclei. Above 20% deformation not only do the original grain-boundaries move, but new nuclei form in the environment of these grain-boundaries (fig. 3) and above 30% deformation additional grain-boundaries form in the interior of the grains by rearrangement of dislocations; (c) by increase of $t_P - t_R$, an increasing volume portion is already recrystallised before precipitation starts.
(iii) $t_R = t_P$ and discontinuous precipitation occurs. The moving grain-boundary leads to simultaneous annihilation of dislocations and precipitation from the supersaturated solid solution. In this way a higher driving force $P_N + P_C$ originates. This case is observed in alloy 4, $10\% < \epsilon < 20\%$ (fig. 6). However, this reaction does not sweep through the whole volume because P_C decreases and P_P increases after the start of continuous precipitation, which leads to a deceleration of the reaction front. The reaction stops, if $P_N + P_C - P_P \leq 0$ (fig. 6d). In fig. 8 the time-dependence of the forces is shown in a schematic way.

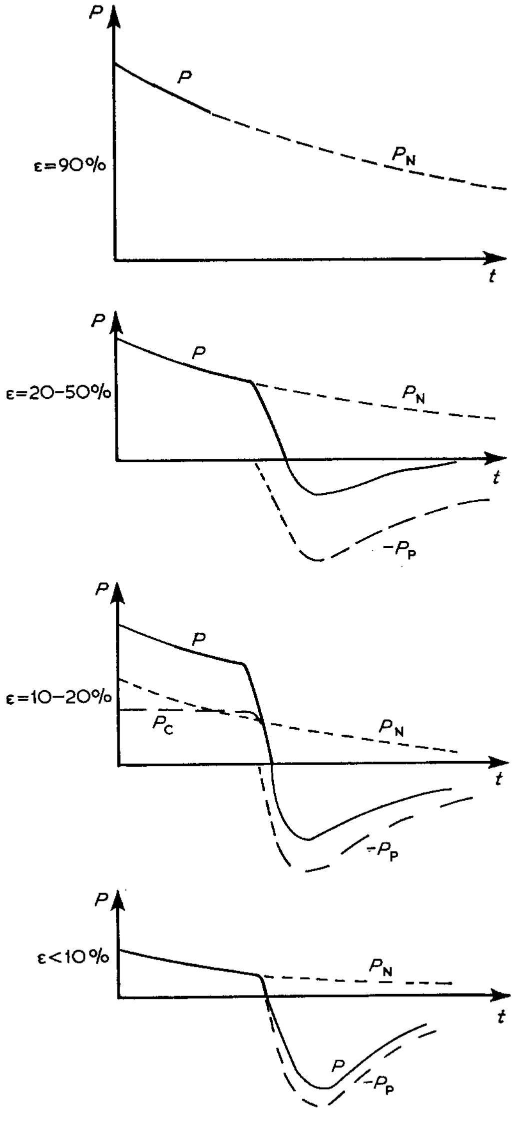


Figure 8 Schematic sketches of time-dependence of force P, acting on a grain-boundary for different degrees of deformation, P_N driving force generated by dislocations, P_C chemical driving force, P_P pinning force produced by particles, $P = \Sigma P_i$, T = constant.

Similar considerations can be applied to any alloying system, if the precipitation behaviour and the interaction between the precipitate phase and grain-boundaries are known. Not all particles are stable in respect to the grain-boundary, they can be dissolved along the grain-boundary (Ni-Al: Ni_3Al particles with $r < 100$ Å) or transformed (metastable $\theta' \rightarrow$ stable phase θ, Al-Cu). In these cases the forces P_C and P_P have to be modified correspondingly.

5. Summary

Recrystallisation of supersaturated copper-cobalt solid solutions has been investigated as a function of supersaturation and the amount of deformation by light and electron microscopy. In the alloy with 2.8 at. % cobalt, recrystallisation is influenced by precipitation of the second phase up to an amount of deformation $\epsilon = 50\%$.

For $\epsilon < 10\%$ precipitating particles inhibit recrystallisation. For $10\% < \epsilon < 20\%$, precipitation and recrystallisation occur simultaneously moving portions of original grain-boundaries. Precipitation and recrystallisation lead to forces on the grain-boundaries of the same sign.

For $20\% < \epsilon < 50\%$ new recrystallisation nuclei are formed; particles precipitated in front of the reaction front retard the motion of the grain-boundaries. At higher amounts of deformation or smaller cobalt contents, recrystallisation is already complete before precipitation starts.

From a knowledge of the interaction of particles with dislocations and the forces acting on grain-boundaries, the temperature and concentration ranges in which the different phenomena occur can be derived.

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